LINEAR POLYMERS CONTAINING BICYCLIC STRUCTURES FORMED BY A CYCLOPOLYMERIZATION MECHANISM

By

MARION LAWRENCE MILES

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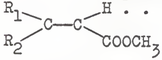

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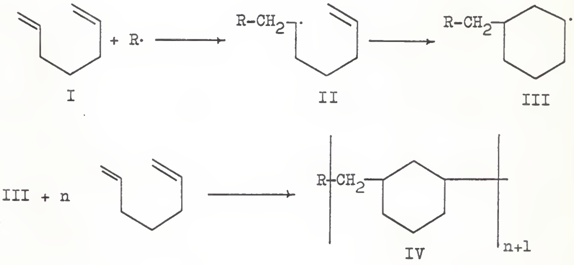
CHAPTER I

INTRODUCTION

History of Intramolecular-Intermolecular Polymerization

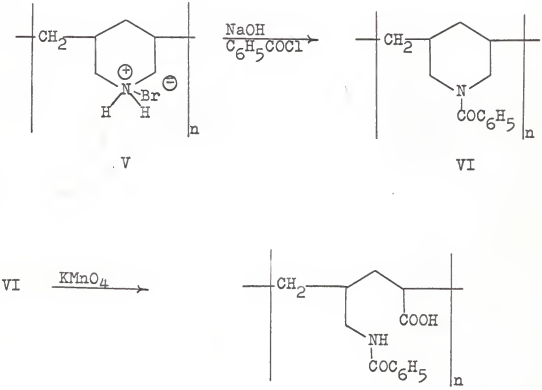
Intramolecular-intermolecular polymerization (cyclopolymerization) is a polymerization mechanism for non-conjugated dienes in which one double bond reacts with the initiator, and the resulting cation, anion or free radical attacks the other double bond in an intramolecular step thereby furnishing a new reaction site, which in turn attacks an adjacent monomer molecule thus propagating the reaction to form a linear polymer containing cyclic units. This mechanism (1) can be illustrated as follows:



I II III IV

Whether the reaction proceeds stepwise as depicted above or in a concerted manner has not been reported.

Since the early work of Staudinger and Heuer (2) it has been generally accepted that monomers containing two or more isolated double bonds would polymerize to form a three-dimensional crosslinked network. In 1951, Butler and Ingley (3) reported that in the course of attempting to prepare some new strongly basic ion exchange resins they had occasion to polymerize a diallyl quaternary ammonium salt in the presence of catalytic quantities of tert-butylhydroperoxide. The resulting polymer was water soluble -- a property not normally associated with crosslinked polymers. The monoallyl derivatives did not polymerize under similar free radical conditions, while the corresponding monomer containing three or four allyl groups gave water insoluble crosslinked polymers which were strong anionic exchange resins. Upon further investigation the polymers derived from the diallyl quaternary ammonium salts were found to contain cyclic units. Since the first polymers of this type to be studied were poly(diallyldialkylammonium bromides), a study was made to determine whether or not this new polymerization mechanism was brought about by the steric influence exerted by the two alkyl groups causing a more favorable intramolecular step. It was found, however, that diallylamine hydrochloride also polymerized by this mechanism, hence steric assistance was not necessary for cyclization to occur. In order to prove conclusively the presence of a cyclic unit poly(diallylamine hydrobromide) was degraded as follows (4):

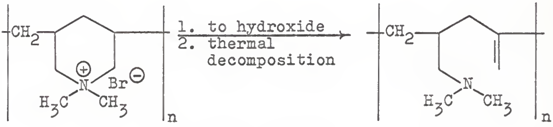


V

VI

VII

The structure of VII was shown to be correct by elemental analysis, potentiometric titration and infrared spectral analysis. On heating VII slightly above its melting point a sublimate of benzoic acid and a crosslinked polymeric material were obtained. Poly(diallyldimethylammonium bromide) was also degraded to yield trimethylamine and a crosslinked polymer residue (4).



VIII IX

$$\text{IX} \quad \xrightarrow[\text{3. thermal decomposition}]{\text{1. } CH_3I \quad \text{2. to hydroxide}} (CH_3)_3N + \text{crosslinked polymer}$$

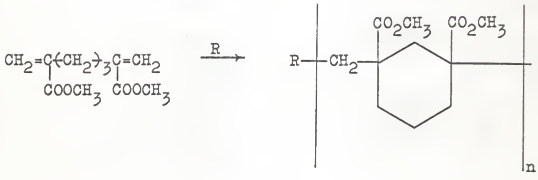
It is apparent that the degradation products from the above two reaction sequences resulted from the cleavage of ring units in the original polymer and are in agreement with the proposed structures.

Previous to Butler's discovery, Walling (5) had postulated that the observed gel points in polymerizing systems should occur somewhat later than calculated by Stockmayer's equation (6), since Stockmayer had omitted statistical perturbations for occasional cyclization. In support of this postulate it was found that for the systems methyl methacrylate-ethylene dimethacrylate and vinyl acetate-divinyl adipate that the ratios of observed to calculated gel points were often as high as 15 to 20.

Simpson, Holt and Zeite (7) studied polymers of diallyl phthalate at the gel points and concluded that approximately 43 per cent of the reacted monomer had been used to form cyclic structures. Haward (8) calculated from purely probability considerations that 31 per cent of the monomer units from this ester would undergo cyclization during polymerization of this material in bulk. Considering the rather crude model used by Haward in calculating this probability, his result is in fair agreement with the experimental value obtained by Simpson, and these workers have extended their work in this direction. Oiwa and Ogata (9) have since been able to obtain 81 per cent cyclization by solution polymerization of diallyl phthalate.

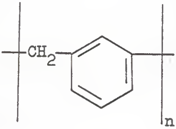
Shortly after Butler's first discussion of this type polymerization at a Gordon Research Conference (10) in 1955, Holt and Simpson (11) offered evidence that polymerizations of other diallyl esters of dibasic acids produced quite a large number of cyclic as well as cross-linked units. Their investigation indicated that the highest degree of cyclization was realized for diallyl carbonate and that as the distance between the double bonds along the chain axis increased the degree of cyclization decreased.

Marvel and Vest (12) have polymerized dimethyl α,α'-dimethylenepimelate using free radical initiation and have found that when polymerization was carried out in bulk a crosslinked polymer resulted. However, if the polymerization was effected in solution, or even in emulsion, the product was completely soluble in a variety of organic solvents. The inherent viscosity of one particular sample of this polymer was as high as 0.73 indicating a rather high molecular weight. By using the constants characteristic of methyl methacrylate and the above viscosity, for instance, they calculated an actual molecular weight of 200,000 to 300,000. The infrared spectrum of this polymer revealed no measurable carbon-carbon unsaturation, and the x-ray diffraction pattern did not indicate any appreciable degree of crystallinity. The properties of this polymer are consistent with a cyclic linear structure analogous to the one proposed by Butler for the diallylammonium derivatives.



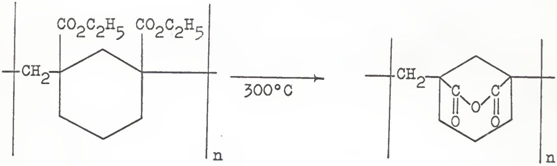
X

As a further confirmation of the cyclic structure, the polymer was dehydrogenated by heating with potassium perchlorate at 390°C. A new soluble polymer was obtained which gave aromatic absorption bands in the infrared (1595 and 1500 cm^{-1}) and also showed ultraviolet absorption (λ_{max} 255 mu) characteristic of m-disubstituted benzene rings.



XI

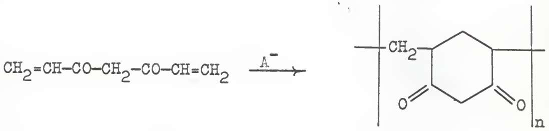
The corresponding polymer from the diethyl ester was pyrolyzed at 300°C to yield a new soluble polymer and ethylene. The new polymer gave infrared absorption bands characteristic of an anhydride, and the degradation may be represented as follows:



XII

XIII

Jones (13) has reported that a polymer containing cyclic units was obtained in an attempt to cause a Claisen condensation to take place between methyl vinyl ketone and ethyl acrylate. The expected product, diacrylylmethane, was apparently formed and rapidly underwent an anionic-initiated intramolecular-intermolecular polymerization to yield a soluble polymer. Structural studies concluded that this polymer contained cyclic diketone units.

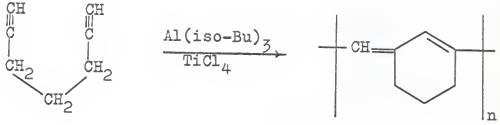


XIV

Marvel and Stille (14) have found that 1,6-heptadiene can be polymerized by Zeigler-type initiators (80% conversion) to give a soluble film-forming polymer which softens at 210-230°C. This polymer was dehydrogenated in a sealed tube at 360-380°C, and the resulting polymer showed aromatic absorption bands in both the infrared and ultraviolet.

Recently Field (15) has been able to polymerize 2,6-diphenyl-1,6-heptadiene by the intramolecular-intermolecular mechanism using thermal, cationic, anionic, free radical and coordination type initiators. All polymers obtained from this monomer were soluble in organic solvents and varied in inherent viscosity from 0.19 to 0.49 with polymer melt temperatures from 140 to 300°C. The best method for obtaining both high conversion and high molecular weight polymer was anionic polymerization using sodium naphthalene as the initiator and tetrahydrofuran as the solvent. Under these conditions an 80 per cent yield of polymer was realized, and this compound had an inherent viscosity in benzene of 0.49 and a polymer melt temperature of 300°C.

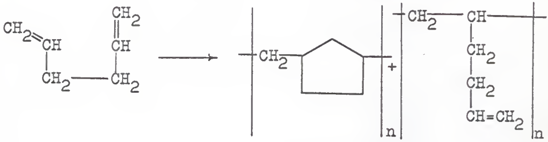
Stille (16) has described the Zeigler initiated polymerization of 1,6-heptadiyne to yield a cyclic polymer of the type under discussion.



XV

Heating the polymer with palladium on charcoal appeared to convert it to polybenzyl.

While most of the early work was done on monomers capable of forming six-membered rings, larger and smaller rings have been reported. Marvel and Stille (14) have polymerized 1,5-hexadiene using a Zeigler catalyst to give an overall 87 per cent conversion. However, only 46 per cent of this material was soluble polymer, and this soluble fraction contained approximately 8 per cent of open chain units each with one double bond.



92-95%

5-8%

XVI

XVII

This material had a rather low polymer melt temperature of 85-90°C and an inherent viscosity of 0.23. Marvel and Gall (17) have found that 2,5-diphenyl-1,6-hexadiene can be reacted to form a soluble polymer of low inherent viscosity by the action of Zeigler, cationic and free radical initiators.

Marvel and Garrison (18) have carried out a thorough investigation on monomers which will polymerize to form larger than six-membered rings. The hydrocarbon monomers incorporated in this study were of the general type $CH_2 = CH(CH_2)_nCH=CH_2$ in which *n* is equal to 4, 5, 6, 7, 8, 9, 11, 12, 14 and 18. All of the polymerizations were conducted using Zeigler catalyst. The results of this study are summarized in Table 1. These percentages of cyclization approximate those realized in other similar type cyclization reactions. That is, seven-membered rings form fairly readily, the intermediate ring sizes with more difficulty, the rings containing 14 or 15 carbon atoms more easily, and finally the yields of cyclic products decrease for the longer carbon chains. All of the soluble polymers were of relatively low molecular weight as indicated by the low viscosities.

Intramolecular-intermolecular polymers incorporating heteroatoms in the cyclic units, other than Butler's original piperidinium salts, have been reported. Butler and Crawshaw (19) and Jones (20) have described, independently, the polymerization, under a variety of conditions, of acrylic anhydride to give linear polymers which are soluble in several organic solvents. The polymers obtained by Butler and Crawshaw gave intrinsic viscosities from extremely low values (ca. 0.04) up to 1.95, and by making use of the constant from the equation relating intrinsic viscosity to degree of polymerization for polyacrylic acid, they calculated molecular weights for these polymers in the range of > 5,000 to 95,000. Butler and Stackman (21) and Marvel and Woolford (22) have

TABLE 1

POLYMERIZATION OF HIGHER DIENES WITH METAL ALKYL COORDINATION CATALYST

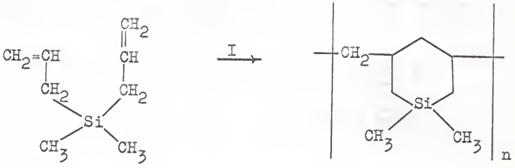
Monomer (0.2M) $CH_2=CH(CH_2)_nCH=CH_2$	Smallest Possible Ring Size	Estimated Cyclic Units in Soluble Polymers (%)	Conversion (%)		Inherent Viscosity of Soluble Polymer[a]
			Soluble	Insoluble	
n = 4	7	25	54	2	0.048
n = 5	8	9	20	40	.14
n = 6	9	6	18	38	.12
n = 7	10	10	25	41	.058
n = 8	11	11	27[b]	40	.086
n = 9	12	11	25[b]	36	--
n = 11	14	15	38[b]	32	.062
n = 12	15	15	17	57	.16
n = 14	17	4	40[c]	22	.055
n = 18	21	8	38[b]	37	.066

[a] The inherent viscosity of the soluble polymers was determined at 25°C at a concentration of 0.25 g./100 ml. in benzene.

[b] 0.05M monomer concentration.

[c] 0.6M monomer concentration.

polymerized diallyldimethylsilane and diallyldiphenylsilane using both Zeigler-type catalyst and free radicals as initiators and obtained soluble polymers.



XVIII

The weight-average molecular weight for poly(diallyldiphenylsilane), as determined by light scattering measurements, was 60,000. A value of 0.065 was found for the intrinsic viscosity in benzene solution. Butler, Skinner and Stackman (23) have described soluble polymers from diallyldialkylphosphonium salts by free radical initiation. Cyclic polymers have also been reported for the polymerization of diallylphenylphosphine oxide, dimethallylphenylphosphine oxide and allylphenyl allylphosphonate (24).

In addition to the types of monomers already described which undergo intramolecular-intermolecular polymerization, an investigation has been made using unsymmetrical monomers which could theoretically polymerize by this mechanism. Because of the copolymerizing tendencies of maleate and furmarate esters, unsaturated esters of these acids having the requisite diene structure have been prepared, polymerized and the resulting polymers studied (25). The allyl, crotyl and 3-butenyl esters of the monomethyl esters of these acids were found to yield cyclic polymers. Tables 2 and 3 summarize the results of this study.

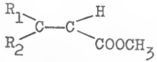
Structural studies on these polymers indicate that five-, six- and seven-membered lactone rings were formed during the polymerizations.

Table 4 lists all the monomers reported up to the present time which undergo intramolecular-intermolecular polymerization.

As might be expected, 1,4-dienes are capable of copolymerizing with certain olefins to produce linear polymers containing cyclic units. Divinyl ether and maleic anhydride constitute just such a pair and have been copolymerized (39) using a free radical initiator to form a polymeric anhydride containing tetrahydropyran rings according to the following sequence:

TABLE 2

PHYSICAL PROPERTIES OF POLYMERS OF



Compound	R_1	R_2	Softening Point (°C)	Inherent Viscosity (at conc., g./100 ml.)
Ia	H	$-COOCH_2CH{=}CH_2$	95	0.061(0.306)
Ib	H	$-COOCH_2-CH{=}CHCH_3$	110	0.036(0.297)
Ic	H	$-COOCH_2-CH_2CH{=}CH_3$	105	--
IIa	$-COOCH_2-CH{=}CH_2$	H	100	--
IIb	$-COOCH_2-CH{=}CHCH_3$	H	75	0.044(0.243)
IIc	$-COOCH_2CH_2-CH{=}CH_3$	H	100	0.072(0.262)

TABLE 3

GEL TIMES, PER CENT CONVERSION AT GELATION, CATALYST-TO-MONOMER RATIO AND PER CENT CYCLIZATION

Polymer	Gel Time (hrs.)	Conversion at Gelation (%)	Benzoyl Peroxide as % of Monomer	Approximate Cyclization (%)
Poly-Ia	9	18	2	49
Poly-Ib	[a]	28[a]	2	60
Poly-Ic	8.25	12	2	38
Poly-IIa	11.5(1)[b]	9	0.1	63
Poly-IIb	56	17	2	23
Poly-IIc	12(1)[b]	14	0.1	43

[a] No gelation after 243 hours. The per cent conversion at gelation represents the yield soluble polymer after this period of heating at 62°C.

[b] Using 2 per cent benzoyl peroxide.

TABLE 4

MONOMERS WHICH POLYMERIZE BY THE INTRAMOLECULAR-INTERMOLECULAR MECHANISM

Monomers	Concentration of Monomers (moles/liter)	Yield of Polymer (%)	Soluble Polymer (%)	Cyclic Soluble Polymer (%)	Reference
Acrylic anhydride	bulk	100	100	98.6-100	19,20
Alloocimene	2.8	84	100	90	26
Allyl acrylate		60	100	58.6	27
Allyl crotonate	bulk	10		25[a]	25
Allylphenyl allylphosphonate	bulk	15-28	100	100	24
2-Carboethoxybicyclo [2.2.1] 2,5-heptadiene				100	28
Diacrylylmethane		100	100	100	13
Diallylammonium chloride	3	94	100	100	4
Diallyldi^{m}ethylammonium bromide	3	66	100	100	1
Diallyldimethylsilane	0.8-2.3	7-91	94-100	94-100	21,22
Diallyldiphenylsilane	1.3-1.6	25-56	100	100	21
Diallylphenylphosphine oxide	bulk	16-31	100	100	24
Diallyl phthalate	bulk	7-22	100	43	7,9

TABLE 4-Continued

Monomers	Concentration of Monomers (moles/liter)	Yield of Polymer (%)	Soluble Polymer (%)	Cyclic Soluble Polymer (%)	Reference
N,N-Diallyl melamine	bulk	9-92		99	29
2,6-Dicyano-1,6-heptadiene	0.6-1.6	4-24	100	100	30,31
Diethyl- α,α'-dimethylene pimelate	0.08	96	100	100	12
Dimethallylethylphosphine oxide	bulk	4-5	100	100	32
Dimethallylmethylphosphine oxide	bulk	15	100	-	32
Dimethallylphenylphosphine oxide	bulk	11-18	100	100	24
Dimethyl-α,α'-dimethylene adipate		18	100	90	30
Dimethyl-α,α'-dimethylene pimelate	0.5-1.2	22-100	100	100	12
2,5-Dimethyl-1,5-hexadiene	2.5-2.7	100	100	87-97	14
1,4-Dimethylenecyclohexane	2.7	85	100	96	33
α,α'-Dimethylenepimelic acid	0.25	54	100	100	12

TABLE 4–Continued

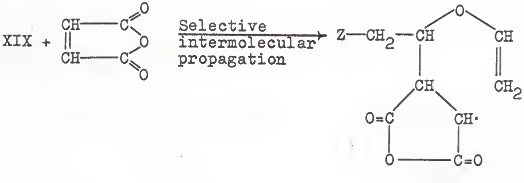
Monomers	Concentration of Monomers (moles/liter)	Yield of Polymer (%)	Soluble Polymer (%)	Cyclic Soluble Polymer (%)	Reference
3,6-Dimethyleneoctadiene-1,7	0.5	50	74	-	34
2,6-Diphenyl-1,6-heptadiene		36-94	100	100	15
Divinyl butyral		24-82	100	-	35
Divinyl ethanol		35-75	100	-	35
Divinyl formal		40	100	-	35
1,3,9,11-Dodecatetraene	0.6	17-35	47	-	34
1,6-Heptadiene	1.9-6.2	50-80	100	90-96	14
1,5-Hexadiene	2.8-5.9	1-87	46	92-95	14
1,6-Heptadiyne	3.1	0-90	10	100	16
1,7-Octadiyne	2.7	84	49	100	16
1,8-Nonadiyne	2.4	92	22		16
β-Methallyl crotonate	bulk	10	-	31	25
Methallyl maleate	bulk	18	-	49	25
Methyl-2-butenyl maleate	bulk	28	100	60	25
Methyl-3-butenyl maleate	bulk	12	-	38	25

TABLE 4-Continued

Monomers	Concentration of Monomers (moles/liter	Yield of Polymer (%)	Soluble Polymer (%)	Cyclic Soluble Polymer (%)	Reference
Methallyl fumarate	bulk	9	-	63	25
Methyl-3-butenyl fumarate	bulk	14-17	-	23-43	25
2-Methyl-1,4-hexadiene-3-one			-	50	36
Myrcene	1.1	2-63	-	91	37
1,3,8-Nonatriene	1.7	23	43	98	38
1,3,6,8-Nonatetraene	.6	17	50	-	34

$$CH_2{=}CH{-}O{-}CH{=}CH_2 + Z\cdot \longrightarrow Z{-}CH_2{-}\dot{C}H{-}O{-}CH{=}CH_2$$

XIX



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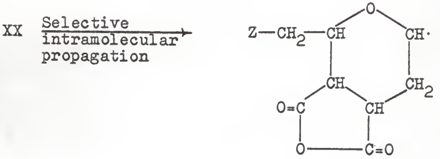
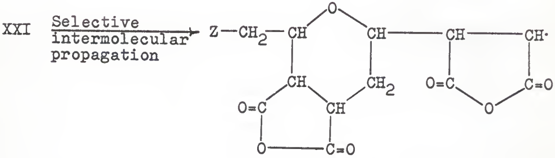


XXI



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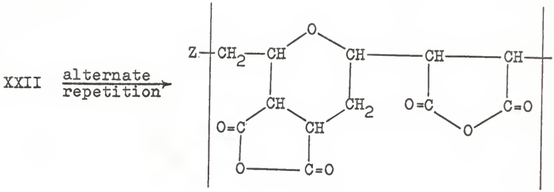
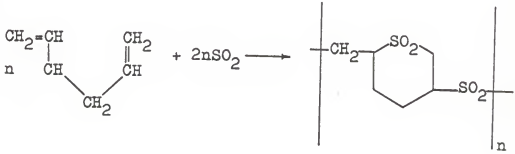


XXIII

The copolymer is soluble in acetone, dimethylformamide (DMF) and aqueous sodium hydroxide. It has a melting point of 350°C, an intrinsic viscosity of 0.175 in DMF and undergoes the usual reactions of anhydrides. Table 5 lists additional comonomers which form polymers of this type (39).

An interesting copolymerization, which has been briefly studied (40), involves the addition of 1,5-dienes to molecules such as sulfur dioxide which are capable of undergoing insertion type reactions.



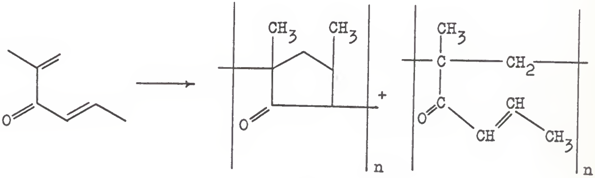
XXIV

TABLE 5

COPOLYMERS OF 1,4-DIOLEFINS AND MONOOLEFINS

1,4-Diolefin	Monoolefin	Intrinsic Viscosity in DMF
Divinyl ether	Furmaronitrile	--
Divinyl ether	Dimethyl fumarate	0.123
Divinyl ether	Diethyl maleate	0.235
Divinyldimethylsilane	Maleic anhydride	0.121
Divinyldimethylsilane	Fumaryl chloride	0.142
Divinyldimethylsilane	Vinyl acetate	0.063
Divinylcyclopentamethylenesilane	Maleic anhydride	0.106
Divinyl sulfone	Maleic anhydride	0.064

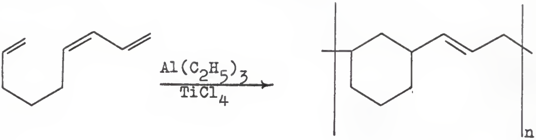
Matsoyan (36) has published a paper on the polymerization of 2-methyl-1,4-hexadiene-3-one. This compound gave a soluble polymer which was approximately 50 per cent cyclic, and spectroscopic examination indicated the presence of 2,4-dimethylcyclopentane rings. Structural confirmation was determined by ozonolysis, which produced acetic acid and a polymeric acid whose neutralization equivalent corresponds to approximately two monomer units per carboxyl group.



XXV 50%

XXVI 50%

More recently, Brooks (38) has described Zeigler catalyzed polymerizations of cis and trans-1,3,8-nonatrienes. The cis isomer was converted, in low yield, to an insoluble rubbery polymer, but the trans moiety was polymerized to yield a material of which approximately 43 per cent was soluble in hot benzene. The soluble portion gave an infrared spectrum consistent with a linear polymer containing cyclic units.



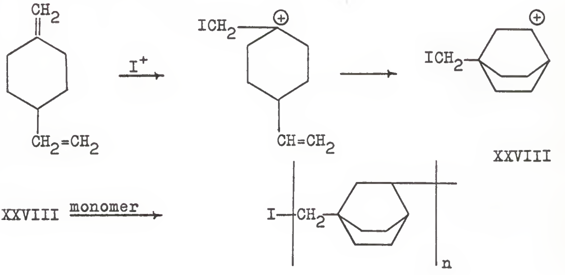
XXVII

Raymond (34) has presented evidence which indicates that even though both double bonds involved in the intramolecular step are themselves a part of a conjugated system some degree of cyclization will occur. He has succeeded in isolating soluble polymers from Zeigler catalyzed polymerizations of 1,3,9,11-dodecateraene, 1,3,6,8-nonatetraene and 3,6-dimethyleneoctadiene-1,7.

In summary, 1,6-dienes will generally polymerize predominately by the intramolecular-intermolecular mechanism to yield soluble polymers incorporating cyclic units, while 1,5- and 1,7-dienes will respectively polymerize to give five- and seven-membered ring repeating units, but do so less readily, and their polymeric products will contain some open chain unsaturated groups. Rings larger than seven-membered may be formed by this mechanism, but the tendency to form these cyclic units drops markedly.

Statement of the Problem

Although there has been a large volume of research carried out involving the intramolecular-intermolecular polymerization mechanism, cyclic 1,5- and 1,6-diene monomers have not been appreciably investigated. Such monomers would presumably lead to linear saturated polymers containing bicyclic units incorporated in the chain backbone as illustrated below.



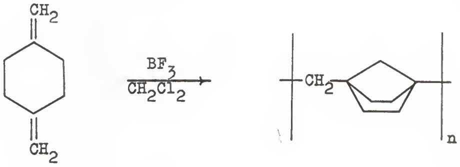
XXVIII

XXVIII

XXIX

These bicyclic polymers should have interesting and perhaps valuable physical properties.

The purpose of the present research was to investigate this area by preparing the requisite monomers, polymerizing these compounds and ascertaining whether or not the resulting polymers contained bicyclic units. While this work was in progress, Ball and Harwood (33) presented a paper concerning the cationic polymerization of 1,4-dimethylenecyclohexane to yield a soluble polymer with the desired bicyclic units.



XXX

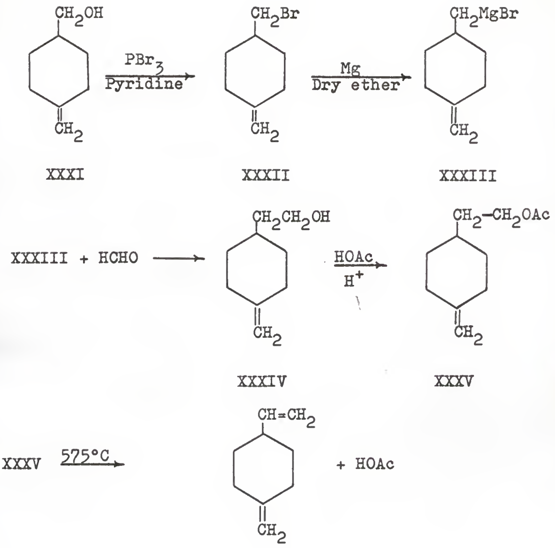
CHAPTER II

DISCUSSION AND RESULTS

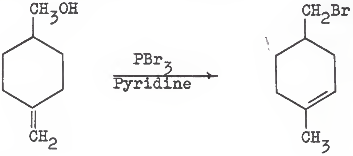
Syntheses Related to Monomer Preparations

For the purposes of the present research, it was necessary to obtain cyclic dienoid monomers which are structurally capable of undergoing cyclopolymerization to yield linear polymers containing bicyclic units. Of the wide variety of monomers which meet these requirements, an accessibility limitation is, of course, imposed, and even for the simpler structures this was a rather formidable obstacle. Development of the synthetic routes to the desired monomers constituted the major portion of the experimental work. Fortunately, one of the monomers, 4-vinylcyclohexene, was available commercially but the other three, 4-methylene-1-vinylcyclohexane, 2-allyl-1-methylenecyclohexane and cis-1,3-divinylcyclopentane, were not obtainable from commercial sources.

The original proposal for the synthesis of 4-methylene-1-vinylcyclohexane was by the following five-step reaction sequence.



In attempting to carry out the conversion of the initial alcohol (XXXI) to the corresponding bromide (XXXII), according to the procedure developed by Gaubert, Linstead, and Rydon (41) for unsaturated alcohols, a 78 per cent yield of an alkyl bromide was obtained. However, infrared spectral analysis revealed a very marked decrease in the absorption band at 1690 $cm.^{-1}$ (C = C), and the disappearance of the band at 885 $cm.^{-1}$ ($C = CH_2$) . The absence of strong bands at these positions indicated that the product obtained from this reaction was not the desired alkyl halide. This compound took up bromine very rapidly, indicating that a bond migration had taken place, and this fact was confirmed by a nuclear magnetic resonance (NMR) spectrum. This bromide was finally identified as 4-bromomethyl-1-methylcyclohexene.

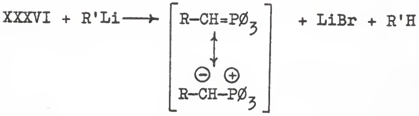


This result is somewhat surprising since this procedure was specifically designed and reported to yield alkyl bromides without double bond migration. A rather large amount of pyridine is used, partly to react with any hydrogen bromide which might be formed during the course of the reaction since, presumably, the bond migration is acid catalyzed. Using this procedure, a solution of the alcohol dissolved in pyridine is added to the phosphorous tribromide in the mole ratios for alcohol, pyridine and tribromide of 3.7:1:1.6, respectively. However, by changing the order of addition so that the alcohol was added to a cold solution of phosphorous tribromide dissolved in pyridine and using the mole ratios of 2.3:3.7:1, in the same order as above, the desired product, 1-bromomethyl-4-methylenecyclohexane, was obtained -- but only in a 5 per cent yield. The structure of this compound was confirmed by elemental, infrared and NMR analyses. Since the acquiring of this bromide was only the first step in a rather long synthesis, this path to the diene was quickly abandoned.

Of the various methods of preparing unsaturated hydrocarbons, the Wittig reaction (42) offers the distinct advantage of giving unrearranged products. The general reaction may be represented as follows:

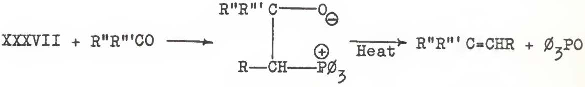
$$\text{R–CH}_2\text{–Br} + \phi_3\text{P} \longrightarrow [\text{R–CH}_2\text{–P}\phi_3]^{\oplus}\,\text{Br}^{\ominus}$$

XXXVI



$$\text{XXXVI} + \text{R'Li} \longrightarrow \left[\begin{array}{c}\text{R–CH=P}\phi_3\\ \updownarrow \\ \overset{\ominus}{\text{R–CH}}\text{–}\overset{\oplus}{\text{P}}\phi_3\end{array}\right] + \text{LiBr} + \text{R'H}$$

XXXVII

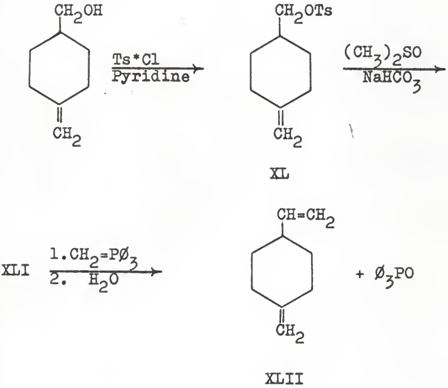


$$\text{XXXVII} + \text{R''R'''CO} \longrightarrow \begin{array}{l}\text{R''R'''C}\text{——}\text{O}^{\ominus}\\ \qquad\quad | \\ \text{R—CH——}\overset{\oplus}{\text{P}}\phi_3\end{array} \xrightarrow{\text{Heat}} \text{R''R'''C=CHR} + \phi_3\text{PO}$$

XXXVIII XXXIX

The C=C linkage is reported to form only at the point where the carbonyl group existed originally.

Synthesis of 1-methylene-4-vinylcyclohexane was finally accomplished by using the Wittig reaction in following sequence.



XL

XLI

XLII

*Ts = *para*-toluenesulfonate

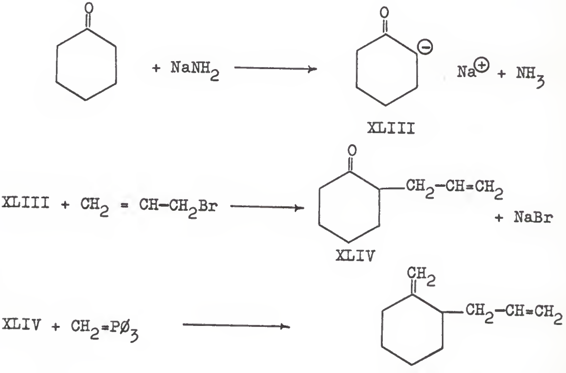
Preparation of the tosylate (XL) was performed according to the method of Marvel and Sekera (43), and this product was of sufficient purity to use directly in the next step.

The subsequent oxidation reaction is an adaptation of a procedure developed by Kornblum (44). The reaction is carried out using dimethyl sulfoxide not only as a part of the oxidizing system but also as the solvent, and even though Kornblum reports rather high yields (60-70 %) for the reaction, these yields are based upon the formation of 2,4-dinitrophenylhydrazones from the aldehydes contained in the reaction mixture. Several different isolation procedures were used for separating the aldehyde from the dimethyl sulfoxide solution. Fractional or steam distillation afforded an overall yield of 20 per cent, but by adding an approximately equal volume of water to the reaction mixture and continuously extracting the resulting solution with diethyl ether, the yield was increased to 33 per cent. An infrared spectrum of this aldehyde has absorption bands at 2720 cm.$^{-1}$(-CHO), 1700 cm.$^{-1}$(CHO), 1650 cm.$^{-1}$(C=C), and 890 cm.$^{-1}$($C{=}CH_2$), which are consistent with the expected structure. Generally, the aldehyde was stored for several weeks and then redistilled just before use in the next step of this sequence.

The reaction between the phosphorane derived from methyltriphenylphosphonium bromide and 4-methylenecyclohexanemethanal proceeded smoothly to give moderate yields of the desired product. The procedure used for this reaction was the one developed by Hauser and coworkers (45). The derived monomer, 1-methylene-4-vinylcyclohexane, took up 1.95 moles of hydrogen per mole of monomer when hydrogenated over reduced platinum oxide catalyst. The

NMR spectrum, using an external benzene standard, has two peaks with chemical shifts located at 1.73 and 2.21 parts per million (ppm) and a larger peak at 4.73 ppm. The integrated peak area ratio for sp^2 to sp^3 hydrogens was 1:2 (theoretical 5:9). Gas-liquid chromatographic (GLC) analysis gave only one large peak, using two different columns, indicating a high degree of purity. The infrared spectrum of this compound, run as a pure liquid, revealed the following absorption bands which are assignable to the proposed structure (46): 1643 cm.$^{-1}$(C=C), 995 cm.$^{-1}$ (CH=C), 910 cm.$^{-1}$(-CH=CH_2), 885 cm.$^{-1}$(C=CH_2).

Synthesis of 2-allyl-1-methylenecyclohexane for this study was accomplished via the following sequence of reactions.



XLIII

XLIV

XLV

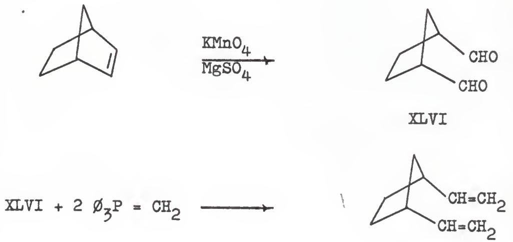
The first two steps in the above set of reactions were carried out using the procedure of VanderWerf and Lemmerman (47), and 2-allylcyclohexanone was obtained in a reasonably good yield.

The initial attempts to perform the third step via the Wittig reaction according to the procedure of Hauser were completely unsuccessful. However, by switching solvents, from diethyl ether to tetrahydrofuran and by refluxing the reaction mixture containing the complex analagous to structure XXXVIII, a high yield of the diene was realized. The NMR spectrum of this monomer is quite complex, but there is a series of peaks bounded by 4.3 and 5.5 τ and another series bounded by 7.8 and 8.5 τ. These field strengths are generally assigned to sp^2 and sp^3 hydrogens, respectively, for compounds of this type. The integrated peak areas ratio for these two sets of peaks are sp^2 to sp^3 of 5:11 (theoretical 5:11).

This compound consumed two moles of hydrogen per mole of monomer when hydrogenated over a rhodium on alumina catalyst and revealed infrared absorption bands in agreement with the assigned structure as follows: 1645 cm.$^{-1}$ (C=C), 990 cm.$^{-1}$(CH=C), 910 cm.$^{-1}$($CH=CH_2$), 890 cm.$^{-1}$($C=CH_2$).

The monomer cis-1,3-divinylcyclopentane was of special interest since both double bonds should have identical reactivity toward the polymerization catalyst.

This compound was prepared by the following two-step synthesis.



XLVI

XLVII

In the second step, the method of Hauser again failed, but the procedure used for the preparation of 2-allyl-1-methylenecyclohexane was successful. The structure and high degree of purity of this compound was established by quantitative hydrogenation, NMR, infrared, GLC and elemental analyses.

In unsuccessful attempts to prepare other monomers for this study, some results were obtained which are sufficiently interesting to be included in this discussion.

Since all of the monomers of interest for the present work contained terminal double bonds, an intense investigation was carried out seeking a general method for substituting a methylene group at this position. As mentioned earlier, the Wittig reaction is very effective for this type placement and has been used extensively for this purpose. The normal procedure for preparing compounds possessing the terminal or exocyclic methylene group by this reaction is via condensation of methylidenetriphenylphosphorane with a compound containing a carbonyl group. However, no investigation had been reported of the converse of this reaction, that is, by condensation of alkyltriphenylphosphoranes with gaseous formaldehyde. Since organic halides are usually more accessible than the corresponding carbonyl compounds, especially the aldehydes, a facile substitution of this type would certainly diversify the Wittig synthesis.

It was found that terminal olefins could be readily obtained by this new method, and subsequently three olefins were prepared in slightly reduced yields than those realized by the older procedure. Hauser (45), in this laboratory, has extended this method even further by using paraformaldehyde as the carbonyl function and obtained comparable yields to those realized by the gaseous formaldehyde procedure. In comparing these two new methods, it should be pointed out that the use of paraformaldehyde offers a simplified experimental procedure but requires a much longer reaction time. The experimental results for these two methods are summarized in Table 6.

TABLE 6

OLEFINS SYNTHESIZED FROM FORMALDEHYDE OR PARAFORMALDEHYDE

Olefin	Phosphonium Salt	Aldehyde	Yield (%)	Boiling Point (°C)
1-heptene	*n*-hexyltriphenylphosphonium bromide	CH_2O	47	93-94
1-octene	*n*-heptyltriphenylphosphonium bromide	$(CH_2O)_n$	42	121-122
styrene	benzyltriphenylphosphonium bromide	CH_2O	64	52-53/27 mm.
styrene	benzyltriphenylphosphonium bromide	$(CH_2O)_n$	65	52-53/27 mm.
styrene	benzyltriphenylphosphonium chloride	$(CH_2O)_n$	75	52-53/27 mm.
2-methyl-1-octene	2-octyltriphenylphosphonium bromide	$(CH_2O)_n$	52	142-143
1,6-heptadiene	pentamethylene-*bis*-(triphenylphosphonium bromide)	CHO	45	89-90
p-divinylbenzene	*p*-xylyl-*bis*-(triphenylphosphonium chloride)	$(CH_2O)_n$	42	62-63/6 mm.

An attempt was made to prepare cis-1,3-divinylcyclohexane by this method. However, this preparation was unsuccessful primarily due to an inability to form the diphosphonium salt of the corresponding dibromide. The mono salt was made, and some olefinic material was prepared, but the yields were prohibitively low to run two successive Wittig reactions to obtain the desired monomer.

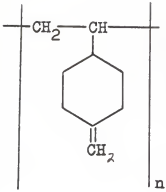
Polymerizations

Excluding cis-1,3-divinylcyclopentane, attempts were made to polymerize the monomers discussed in the previous section by free radical, metal alkyl coordination catalysts of the Zeigler-type, anionic and cationic initiators. Substantial yields of polymers were effected only for Zeigler catalyst and cationic initiators, and in view of the fact that these monomers do not incorporate any activating groups for the other two types of initiation, these results were anticipated.

The NMR spectra of all the soluble polymers isolated in this study were very similar and appropriately should be discussed together. The peak for the sp^3 bonded hydrogens was very broad and occurred at a chemical shift of approximately 8.6 $\tau \pm 1\ \tau$ while the sp^2 bonded hydrogens usually gave rise to two peaks at approximately 4.5 and 5.2 τ.

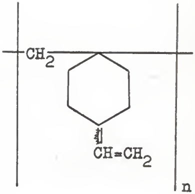
X-ray diffraction studies on these polymers did not indicate any appreciable degree of crystallinity.

The polymers obtained from polymerization of 1-methylene-4-vinylcyclohexane using gaseous boron trifluoride as the cationic initiator were white powdery materials which had rather low polymer melt temperatures. Polymerizations by this method at -70°C led to low conversion, but the material obtained from this low temperature reaction contained a high percentage of soluble polymer. The soluble fraction had a polymer melt temperature of 130°C and an intrinsic viscosity of 0.06 indicating a low molecular weight. It was found, however, that by running the polymerization at -70°C for one hour and then allowing the reaction mixture to warm slowly to room temperature the yield of polymer could be increased to 79 per cent. Approximately 70 per cent of this material was soluble in benzene. An infrared spectral analysis of this soluble portion indicated some residual terminal unsaturation. An NMR spectrum gave a ratio of sp^2 to sp^3 bonded hydrogens of 1:7.5 which is not consistent with a polymerization by only one type olefinic group to yield a linear polymer. The structures of some of the various polymer possibilities, along with the corresponding sp^2 to sp^3 hydrogens ratios are as follows:



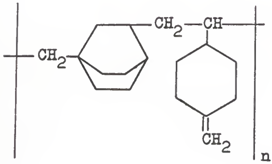
XLVIII

$sp^2:sp^3 = 1:6$



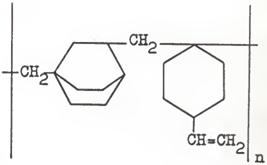
XLIX

$sp^2:sp^3 = 1:3.7$



L

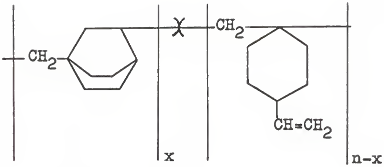
$sp^2:sp^3 = 1:13$



LI

$sp^2:sp^3 = 1:8.3$

The NMR spectrum also indicated that the residual unsaturation was primarily of the vinyl type, and this was confirmed by infrared. This evidence is not consistent with a regular structure such as LI in which the polymer chain is made up of alternating bicyclic units. A more representative structure can be depicted as follows:



LII

The interpretation of this structure is that the polymer chain is made up of bicyclic and cyclic units but in an unknown order.

If the NMR peak area ratio is used for the basis of a per cent cyclization calculation, this polymer gives a value of 40 per cent. It should be clearly understood that this calculation, along with the ones to follow involving cyclization, is only a good approximation and is not based on highly accurate experimental data.

The polymerization of this monomer with a Zeigler catalyst, triethyl aluminum-titanium tetrachloride, gave a reasonable conversion; however, only 10 per cent of the polymer was soluble in hot benzene. The soluble fraction had an intrinsic viscosity of 0.09, and the NMR spectrum indicated a rather high degree of cyclization showing an sp^2 to sp^3 hydrogens ratio of 1:37 (88% cyclization). Infrared spectra of both the soluble and insoluble fractions show some residual unsaturation.

Replacing triethyl aluminum by triisobutyl aluminum in this system led to decreased yields, and the polymers obtained from this initiation appeared to be almost identical to the ones from the triethyl aluminum system.

Although no attempt was made to determine optimum conditions for the polymerization of this monomer, some variation in the reaction conditions were conducted. Table 7 summarizes these conditions and the yields obtained.

For the Zeigler system, aging of the catalyst at different temperatures does not appear to have a significant affect on the yield. However, in this type initiation the ratio of titanium tetrachloride to triethyl aluminum does affect the yield, and the best results were realized using an abnormally high mole fraction of the titanium compound.

Polymerization of 1-allyl-2-methylenecyclohexane with gaseous boron trifluoride initiation did not give as high a per cent conversion as in the case of the previous monomer, but the resulting polymers were almost completely soluble in a variety of organic solvents. The reaction proceeds smoothly at low temperature to give higher yields than the procedure using the rising temperature technique. By using a low temperature and relatively long reaction times, a 44 per cent conversion was obtained, and 94

TABLE 7

1-METHYLENE-4-VINYLCYCLOHEXANE POLYMERIZATIONS[a]

Polymer Number	Solvent (ml.)	Initiator		Catalyst Aging		Reaction Conditions		Polymer	
		System	Conc. (mmoles)	Temp. (°C)	Time (min.)	Temp. (°C)	Time	Yield (%)	Soluble (%)
	None	Benzoyl peroxide	0.02			68	7 days	None	
	None	Benzoyl peroxide	.02			120	14 days	None	
	THF,10	Li-naphthalene	.04			R.T.	20 hrs.	None	
	THF,10	Na-naphthalene	c			R.T.	16 hrs.	None	
	n-Heptane,12	$TiCl_4$ $Al(C_2H_5)_3$	.085 .15	0	45	0 then R.T.	6 hrs. 40 hrs.	0.3	
	n-Heptane,5	$TiCl_4$ $Al(C_2H_5)_3$	.085 .15	98	5	R.T.	7 days	1	
7a	n-Heptane,5	$TiCl_4$ $Al(C_2H_5)_3$	.17 .11	98	5	R.T.	7 days	11	20[b]
7b	n-Heptane,5	$TiCl_4$ $Al(C_2H_5)_3$	.17 .11	R.T.	20	R.T.	14 days	61[d]	10

TABLE 7-Continued

Polymer Number	Solvent (ml.)	Initiator		Catalyst Aging		Reaction Conditions		Polymer	
		System	Conc. (mmoles)	Temp. (°C)	Time (min.)	Temp. (°C)	Time	Yield (%)	Soluble (%)
7c	*n*-Heptane,5	$TiCl_4$	.17						
		$Al(C_2H_5)_3$	.11	0	20	R.T.	18 days	33	12
	n-Heptane,5	$TiCl_4$	.15	R.T.	5	R.T.	6 days	Trace	
		Al(*i*-Bu)$_3$	.15						
7d	*n*-Heptane,5	$TiCl_4$	.17						
		Al(*i*-Bu)$_3$	.11	R.T.	20	R.T.	18 days	10	30[b]
7e	CH_2Cl_2,5	BF_3	gas			-70	24	5	95[b]
7f	CH_2Cl_2,5	BF_3	gas			-70 then R.T.	1 hr. 4 hrs.	79	70

---

[*] R.T. = room temperature.

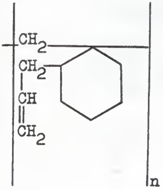
[a] All polymerization carried out using 7.4 millimoles of monomer except where indicated.

[b] Total yield of polymer was too small to determine this percentage accurately.

[c] A solution of approximately 0.1M was prepared of the catalyst in THF. After the monomer and solvent had been placed in the reaction flask, the catalyst solution was injected until the faint bluish color persisted.

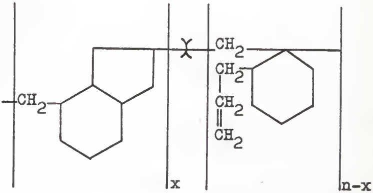
[d] Polymerization carried out using 14.8 millimoles of monomer.

per cent of the resulting polymer was soluble in cold dichloromethane. Both the infrared and NMR spectra revealed some unsaturation in this polymer. Because of the absence of the 882 cm.$^{-1}$ band and the presence of the 991 cm.$^{-1}$ band in the infrared spectrum and the general shape of the NMR curve, structures containing an exocyclic methylene group were eliminated from the structural proposals for this polymer. The most probable structures are as follows:



LIII

$sp^2:sp^3 = 1:4.3$



LIV

for n=x, $sp^2:sp^3 = 1:9.7$

The observed sp^2 to sp^3 ratio is 1:10.5, and by calculating on the basis of structure LIV ($n \neq x$), 54 per cent of the monomer units have undergone cyclization during the polymerization.

The polymers obtained by Zeigler catalyst initiations were almost completely soluble and gave somewhat higher polymer melt temperatures and intrinsic viscosities. To achieve yields of 30 per cent conversion required very long reaction times. The type of alkyl groups incorporated in the aluminum trialkyl portion of this catalyst did not appear to affect the yields significantly. Infrared spectra of these polymers show only a very slight degree of unsaturation and establish that both methylene and vinyl groups are present with the methylene groups predominating. This result is in marked contrast to the Zeigler catalyst initiation of 1-methylene-4-vinylcyclohexane. An NMR spectrum of this polymer indicated such a small degree of unsaturation that the sp^2 peak area could not be measured accurately relative to the sp^3 area (the ratio is less than 1:100). Table 8 summarizes the polymerization conditions and yields for this monomer.

Polymerization of 4-vinylcyclohexene was accomplished by initiation with boron trifluoride, boron trifluoride etherate and, in one case, with a Zeigler catalyst.

Initiation with gaseous boron trifluoride, using the increasing temperature method, resulted in an extremely tacky polymer which was highly discolored. The low temperature polymerization gave higher yields of a white amorphous polymer which was very soluble in chloroform. The infrared spectrum indicated some unsaturation, but it

TABLE 8

1-ALLYL-2-METHYLENECYCLOHEXANE POLYMERIZATIONS

Polymer Number	Monomer Conc. (mmoles)	Solvent (ml.)	Initiator		Reaction Conditions		Polymer	
			System	Conc. (mmoles)	Temp. (°C)	Time	Yield (%)	Soluble (%)
8a	37	CH_2Cl_2,5	BF_3	gas	-70	46 hrs.	44	94
8b	37	CH_2Cl_2,5	BF_3	gas	-70 then R.T.*	3 hrs. 24 hrs.	10	90
8c	7.4	_n_-Heptane,5	$TiCl_4$ $Al(\underline{i}\text{-}Bu)_3$	0.5 .75	R.T.	29 days	30	95
8d	7.4	_n_-Heptane,5	$TiCl_4$ $Al(Et)_3$	.5 .75	R.T.	29 days	27	94
8e	14.8	_n_-Heptane,5	$TiCl_4$ $Al(Et)_3$	.5 .75	R.T.	7 days	8	80^a
8f	14.8	_n_-Heptane,5	$TiCl_4$ $Al(\underline{i}\text{-}Bu)_3$	.5 .75	R.T.	7 days	9	80^a

TABLE 8-Continued

Polymer Number	Monomer Conc. (mmoles)	Solvent (ml.)	Initiator		Reaction Conditions		Polymer	
			System	Conc. (mmoles)	Temp. (°C)	Time	Yield (%)	Soluble (%)
	7.4	None	AiBN[b]	(5 mg.)	80	7 days	None	
	7.4	*n*-Heptane,5	*n*-BuLi	.6	R.T.	14 days	None	

---

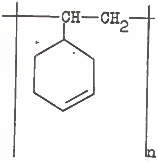
*R.T. = room temperature.

[a] Total yield of polymer was too small to calculate this percentage accurately.

[b] α,α'-azo-*bis*-isobutyronitrile.

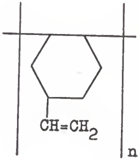
is difficult to make an absolute assignment for the type of unsaturation. At first it was thought that this residual unsaturation was due to occluded monomer, but dissolving and reprecipitating the polymer several times, and then extracting it in a Soxhlet extractor for 54 hours did not decrease the olefin content.

Since the infrared spectral analysis does not allow the exclusion of certain structural possibilities, the interpretation of the sp^2 to sp^3 hydrogens ratio is more difficult and less meaningful, but the NMR data do indicate some cyclization occurred during the polymerization.



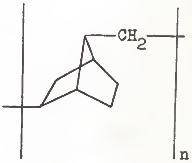
LV

$sp^2:sp^3 = 1:5$



LVI

$sp^2:sp^3 = 1:3$



LVII

The observed $sp^2:sp^3$ ratio is 1:12 and by mixing structures LV and LVII, to agree with the NMR ratio, the degree of cyclization for this polymer would be approximately 50 per cent.

Two experiments were conducted in an attempt to increase the intrinsic viscosity of the polymer by reducing the catalyst concentration for the gaseous boron trifluoride initiation. Usually, the boron trifluoride gas was emitted over a solution of the monomer; the reaction flask was then sealed, and the mixture was left stirring for the remainder of the reaction period. In this set of experiments the gas was emitted and left over the solution for a certain period of time. It was then displaced with dry nitrogen, and the reaction was allowed to proceed for the allotted time. This procedure did not appreciably affect the viscosity, polymer melt temperature or per cent soluble fraction, although it did decrease the yield. This type behavior is consistent with a low degree of polymerization.

Continuous extraction of the chloroform soluble polymer with diethyl ether caused some fractionation to occur. Both the ether soluble and insoluble fractions, however, gave NMR and infrared spectra essentially the same as the non-fractionated polymer.

The polymer obtained from the boron trifluoride etherate initiation was completely soluble in chloroform but gave a low value for the intrinsic viscosity. Again, a high catalyst to monomer ratio was necessary for high conversion. The infrared spectrum of this polymer indicated very little unsaturation, and the NMR spectrum showed an sp^2 to sp^3 ratio of 1:28 (80% cyclization).

The Zeigler catalyst initiation yielded a polymer of which 45 per cent was soluble in chloroform. This soluble fraction was essentially saturated and had a polymer melt temperature of 91°C and an intrinsic viscosity of 0.04. Table 9 summarizes the polymerization conditions and yields for this monomer.

The monomer cis-1,3-divinylcyclopentane was not synthesized until the latter stages of this work, and consequently only a few polymerizations of this compound were attempted. Zeigler catalyst initiation of this monomer using the system triethylaluminum-titanium tetrachloride in the mole ratio of 3:1, respectively, resulted in a 5 per cent yield of polymer. However, by replacing triethylaluminum with triisobutylaluminum and by using a mole ratio of 1:1, a 38 per cent conversion was obtained. Approximately 65 per cent of this polymer was soluble in cyclohexane. An infrared spectrum of this soluble fraction revealed only a trace of unsaturation.

Intramolecular-Intermolecular Mechanism

Although various theories have been proposed to explain the selectivity of the intramolecular propagation step in the reaction under discussion, none of them have

TABLE 9

4-VINYLCYCLOHEXENE POLYMERIZATIONS

Polymer Number	Monomer Conc. (mmoles)	Solvent (ml.)	Initiator		Reaction Conditions		Polymer	
			System	Conc. (mmoles)	Temp. (°C)	Time	Yield (%)	Soluble (%)
9a	14	CH_2Cl_2,8	BF_3	gas	-70 R.T.*	1 hr. then 21 hrs.	5	20[a]
9b	83	CH_2Cl_2,10	BF_3	gas	-70	68 hrs.	20	79
9c	30	CH_2Cl_2,12	BF_3[b]	gas	-70	24 hrs.	9	90
9d	30	CH_2Cl_2,12	BF_3	gas	-70	24 hrs.	28	85
	50	n-Heptane,5	$TiCl_4$	0.85	0	72 hrs.	None	
	12	n-Heptane,2.8	$TiCl_4$	1.7	R.T.	16 days	Trace	
	12	n-Heptane,2	n-ButyLi	3	R.T.	14 days	None	
9e	100	CH_2Cl_2,3	$BF_3(C_2H_5)_2O$	7	0	28 days	35	100
	20	None	AIBN[c]	(10 mg.)	70	14 days	Trace	

TABLE 9-Continued

Polymer Number	Monomer Conc. (mmoles)	Solvent (ml.)	Initiator		Reaction Conditions		Polymer	
			System	Conc. (mmoles)	Temp. (°C)	Time	Yield (%)	Soluble (%)
9f	12	2.2	$TiCl_4$ $Al(\underline{i}\text{-}Bu)_3$	.6 .6	R.T.	14 days	20	45

*R.T. = room temperature.

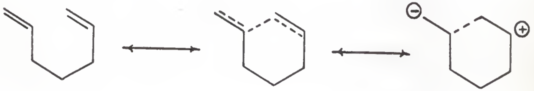
[a] Total yield too small to calculate this percentage accurately.

[b] BF_3 gas was displaced from reaction vessel after a contact time of 15 minutes.

[c] α,α'-azo-bis-isobutyronitrile.

received a widespread acceptance. These theories may be grouped into two general categories: 1) interspatial activated state and/or ground state interactions, and 2) statistical.*

The activated state-ground state interactions theory, put forth by Butler (39) and Raymond (34), is based upon an across space homoconjugation interaction between the double bonds in a monomer molecule. This effect, for 1,6-heptadiene, has been depicted as follows:



LVIII LIX

If 1,6-heptadiene can be appropriately represented by structure LVIII, this molecule would require only a small entropy change in going from the ground state to the activated state for the intramolecular propagation reaction. Aside from this desirable entropy effect, the energy of both the ground and activated states would be decreased.

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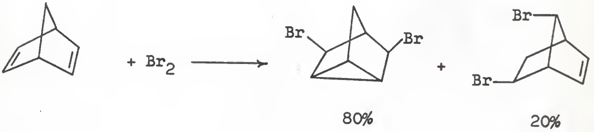
*The first category is, of course, also statistical, but the differentiation used here should be perceived from the discussion which follows.

One would expect such a phenomenon to manifest itself in the ultraviolet region of the spectrum, and Raymond (34) and Brooks (38) have pointed out abnormalities in this spectral region for certain monomers which are known to undergo cyclopolymerization. Brooks interpreted his data in terms of an excited state interaction, whereas Raymond chose to explain his results on the basis of interactions in both the ground and excited states. Winstein (48) has published a paper concerning the ultraviolet spectrum for bicycloheptadiene showing absorption bands at 205 mu (E = 2100), 214 mu (E = 1480), 220 mu (E = 870), and a shoulder at 230 mu (E = 200). By assuming a slight interaction in the excited state, he calculated a theoretical absorption spectrum in good agreement with the observed one. It should be mentioned that this compound adds one mole of such reagents as bromine to yield predominately a saturated product having a nortricyclenic structure (49). The reaction is shown below.



Raymond (34) has given a treatment for the statistical approach to this mechanistic problem. The model for this determination was based on a stepwise mechanism for the polymerization of 1,6-heptadiene. He assumed that a reaction site was formed at the two position and then proceeded to calculate the probability of the number seven carbon being in a volume element surrounding this position.

Treloar (50) had previously solved a similar problem for a one dimensional five-link chain. The carbon-carbon single bond distance was used for the length of each link, and the approximate tetrahedral angle of 109.5° for the angle between links. Treloar allowed completely free rotation about this fixed angle. The graphical solution of this model in terms of the relative probability of specific end-to-end distance is given in Figure 1. Raymond used this distribution function to calculate part of the ratio of intramolecular to intermolecular propagation. He assumed reaction to take place at one bond length and integrated the distribution function between the limits of 0.33 and one bond length. He then calculated the number of double bonds furnished by adjacent molecules within this same volume element. The results obtained by Raymond are given in Table 10. These results could be used to explain the high degree of cyclization in dilute

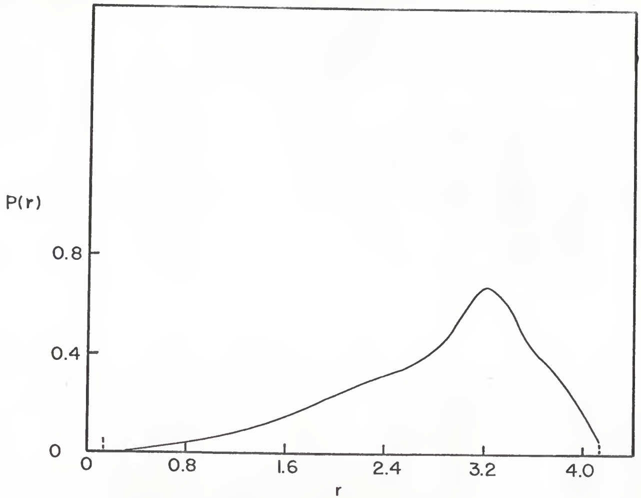


FIGURE 1. DISTRIBUTION FUNCTION FOR LENGTH OF A FIVE-LINK CHAIN

TABLE 10

PROBABILITY OF CYCLIZATION IN 1,6-DIENES

Concentration of Monomer (moles/liter)	$\frac{P_1}{P_2}$	Per Cent Cyclization
7.43	0.34	25
1.00	2.50	71
.10	25.00	96
.01	250.00	99.6
.001	2500.00	ca. 100.0

solution, but they do not correlate with the experimental evidence that this monomer can be polymerized in high concentration (ca. six molar) to yield a polymer which has undergone approximately 90 per cent cyclization.

Returning to the case of the interspatial interaction, the fundamental question is whether or not this phenomenon would necessarily lead to a cyclization step. If this interaction is purely of the across space type, both interactions in the ground and excited states would, presumably, be related only to the distance and orientation of other double bonds with respect to the reaction site. But for polymerization at high concentrations, Raymond has shown statistically that there is a greater probability of a double bond from another monomer molecule to lie within the volume element with a radius of one bond length around the reaction site, than for the other end of this same molecule to lie within this same volume element. It would, therefore, appear that if this explanation is valid it would be primarily due to an orientation effect.

For a strong ππ interaction the nodal planes of all of the p orbitals must lie in a common plane. An examination of a molecular model of 1,6-heptadiene reveals there are two such conformations with a reasonably close approach between the double bonds. One of these conformations is with the closest approach between the number two and number seven carbon atoms, and this is the conformation which could act as a precursor to the formation of a six-membered ring. However, in this geometry one of the terminal hydrogens lies in the nodal plane directly between the number two and number seven carbon atoms. It seems highly unlikely that a $\pi\pi$ interaction could take place through a bonded hydrogen. The other conformation which meets the $\pi\pi$ interaction requirement is with the closest approach between the number two and number six carbons. In this conformation, measurements on a model indicate a closest approach of approximately 2 Å (center-to-center). There is a slight steric interference at this distance from one of the internal chain hydrogens. Of course, the most serious objection to this conformation is that if it leads to ring closure, the resulting ring would be five-membered.

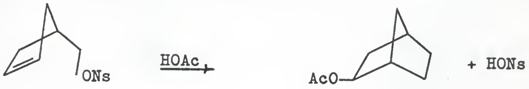
Another type of interaction which is applicable to this molecule is of the so-called $\pi\sigma$ type. In this case the restriction of having the p orbital nodal planes coplanar is removed, and the molecular model indicates that this type interaction, in a conformation which might act as a precursor to the formation of a six-membered ring, is possible.

Since double bonds furnished by other molecules in close proximity to a particular olefinic bond would have, ignoring any induced effects, random orientation, the probability of a given orientation would be controlled by factors beyond the scope of the present discussion.

Another way in which the reaction site might distinguish that one of the many double bonds in its vicinity is unique would be by an inductive effect. It is conceivable that a very weak inductive effect would be operable even at a position four carbons removed from the reaction site. However, this effect would not explain the cyclization since, if this effect was the controlling factor, it would lead to the formation of five-membered rings.

If one assumes a ground state in which there is no interaction, then for the molecule to go from this state to the activated state would involve a relatively large entropy change. This factor would be extremely important in deciding which of two possible reaction paths a reaction would take, assuming an approximately equal activation energy for both paths. Of the two paths for the reaction under consideration, the intramolecular propagation would involve primarily the change in entropy due to rotational degrees of freedom about the various bond axes, whereas the intermolecular step would be primarily concerned with translational motion. A qualitative answer as to the magnitude of these two effects could be derived from the relative contribution of these two modes to the total entropy for molecules of this type in solution.

In recent years, there have been a number of publications concerning a phenomenon that is, in certain respects, similar to the intramolecular-intermolecular polymerization mechanism. Bartlett and Bank (51) have observed that the rate of solvolysis of β-(cyclopentene-3-yl)-ethyl *p*-nitrobenzylsulfonate in acetic acid is 95 times faster than the solvolysis of the corresponding saturated *p*-nitrobenzylsulfonate. The product from the solvolysis of the unsaturated ester is the acetate of *exo*-norborneol-2. The reaction is shown below.



Similar results have been obtained by Closson (52) in open chain systems. He has reported that the solvolysis of 5-hexenyl *p*-nitrobenzylsulfonate in acetic acid yields 34 per cent cyclic and 39 per cent non-cyclic acetate. This reaction is 71 per cent faster than the rate of solvolysis of the *n*-hexyl ester. However, this type ring closure has been demonstrated only in the cases where a carbonium ion is formed during the course of the reaction.

With the experimental data available at the present time, it would be presumptuous to pick one particular effect to explain the intramolecular propagation reaction.

CHAPTER III

EXPERIMENTAL

Equipment and Data

All temperatures herein are uncorrected and reported in degrees centigrade. Pressures are expressed in millimeters of mercury, having been determined by means of either a Zimmerli or McLeod gauge.

Infrared spectra were obtained with a Perkin-Elmer Infracord Double-beam Infrared Recording Spectrophotometer or a Perkin-Elmer Model 21 Double-beam Infrared Recording Spectrophotometer.

Refractive indices were obtained with a Bausch and Lomb Abbe 34 Refractometer equipped with an achromatic compensating prism.

Gas-liquid chromatographic (GLC) analyses were made with a Wilkens Aerograph Model A-110-C Gas Chromatographic Instrument using helium for the eluent gas. Unless otherwise indicated, gas-liquid chromatographic analyses were made on a five-foot column packed with 20 per cent Silicone GE SF-96 on firebrick.

Nuclear magnetic resonance (NMR) spectra were obtained with a Varian V-4302 High Resolution Nuclear Magnetic Resonance Spectrometer.

Melting point determinations of monomeric compounds were carried out in open capillary tubes in a Thomas-Hoover Melting Point Apparatus. The polymer melt temperatures were determined by means of a Kofler micro hot stage.

Intrinsic viscosities were calculated from efflux times of solutions through a Cannon-Ubbelohde Semi-micro Dilution Viscometer set in a 25°C constant temperature bath.

X-ray diffraction spectra were obtained with a Norelco X-Ray Diffractometer Model 12045 using a proportional counter.

Elemental analyses were performed by Galbraith Laboratories, Knoxville, Tennessee.

Source and Purification of Materials

Pyridine and dimethylsulfoxide were obtained from J. T. Baker Chemical Company. The pyridine was distilled before use, and the dimethylsulfoxide was used as received.

4-Vinylcyclohexene was obtained from Cities Service Research and Development Company. This material was dried for 48 hours over anhydrous magnesium sulfate and then distilled immediately before use.

Bicyclo[2.2.1]-2-heptene (norbornylene) was obtained from Aldrich Chemical Company and used as received.

Tetrahydrofuran and cyclohexanone were obtained from Fisher Scientific Company. The tetrahydrofuran was dried over sodium ribbon and then distilled. The cyclohexanone was used as received.

Allyl bromide, triphenylphosphine, titanium tetrachloride and phosphorous tribromide were obtained from Peninsular ChemResearch Incorporated. The allyl bromide and phosphorous tribromide were distilled before use, and the triphenylphosphine and titanium tetrachloride were used as received.

n-Butyl lithium was obtained from Foote Mineral Company and used as received.

Methyl bromide was obtained from Dow Chemical Company and used as received.

4-Methylenecyclohexanemethanol and p-toluenesulfonyl chloride were obtained from Distillation Products Industries division of Eastman Kodak Company. The 4-methylenecyclohexanemethanol was distilled before use and the p-toluenesulfonyl chloride was used as received.

Boron trifluoride (gas) was obtained from The Matheson Company and used as received.

Triisobutyl aluminum and triethyl aluminum were obtained from Ethyl Corporation and used as received.

Syntheses Related to Monomer Preparations

4-Bromomethyl-1-methylcyclohexene.-This compound was prepared by following the procedure outlined by Gaubert, Linstead and Rydon (41) for synthesizing unsaturated alkyl halides. Into a one-liter, three-necked flask, equipped with a reflux condenser which was fitted with a calcium chloride drying tube, mechanical stirrer and an addition funnel was placed 225 g. (0.86 mole) of phosphorous tribromide. The reaction vessel was immersed in an ice-water bath, and a solution of 43.2 g. (0.54 mole) of dry pyridine in 252 g. (2 moles) of 4-methylenecyclohexanemethanol was added dropwise over a period of four hours. The mixture was left at 0°C and stirred for one additional hour and then allowed to warm to room temperature. After stirring at room temperature for 18 hours, the mixture was heated to reflux and maintained at this temperature for 30 minutes. The mixture was then cooled and filtered. The filtrate was washed successively with two 200-ml. portions of water, two 100-ml. portions of a saturated solution of sodium carbonate and finally with two 200-ml. portions of water. The organic solution was dried for 24 hours over anhydrous sodium sulfate. The mixture was distilled at reduced pressure through a 30-cm. vacuum-jacketed Vigreux column. The yield of 4-bromomethyl-1-methylcyclohexene was 378 g. (78%), b.p. 90-92°/1 mm.,

n_D^{25} 1.5057. The product was found by GLC analysis to be approximately 98 per cent pure, and the NMR spectrum agreed with the structural assignment. Infrared analysis revealed the following absorption bands: 2900 cm.$^{-1}$(C-H), 1600 cm.$^{-1}$(C=C, very weak), 1435 cm.$^{-1}$(C-CH_3), 1370 cm.$^{-1}$(C-CH_3), 918 cm.$^{-1}$.

Anal. Calcd. for $C_8H_{13}Br$: C, 50.81; H, 6.92; Br, 42.26. Found: C, 50.61; H, 6.76; Br, 42.49.

1-Bromomethyl-4-methylenecyclohexane.-To 18 g. (0.065 mole) of phosphorus tribromide contained in a 250-ml. three-necked flask which was immersed in an ice-water bath was added dropwise 19 g. (0.24 mole) of dry pyridine over a period of one hour. Thirty-one g. (0.15 mole) of 4-methylenecyclohexanemethanol was added dropwise to the reaction mixture, and then the resulting slurry was stirred for an additional two hours at 0°C. The reaction mixture was heated to reflux, and this temperature was maintained for 30 minutes. After cooling to room temperature, 100 ml. of water were added, and then the mixture was extracted with two 100-ml. portions of ether. The combined ethereal extracts were washed with two 100-ml. portions of a solution of 5 per cent sodium bicarbonate followed by two 100-ml. portions of water. The organic solution was dried over anhydrous sodium sulfate for 24 hours. The ether was removed by distillation at atmospheric pressure, and the residual liquid was distilled at reduced pressure through a 23-plate spinning-band column. The fraction collected at b.p. 96-100°C/16 mm. was refractionated to yield 2 g. of crude product, b.p. 67-69°C/6 mm. This crude material was purified on a silicone preparatory column by GLC. The yield of pure compound was 1.5 g. (5%), b.p. 69-70°/6 mm., n_D^{20} 1.5084. This product was approximately 99 per cent pure by GLC analysis, and the NMR spectrum supported the proposed structure. The infrared spectrum revealed the following absorption bands assignable to the proposed structure: 3072 cm.$^{-1}$(C=CH$_2$), 2900 cm.$^{-1}$(C-H), 1652 cm.$^{-1}$(C=C), 890 cm.$^{-1}$(C=CH$_2$).

Anal. Calcd. for $C_8H_{13}Br$: C, 50.81; H, 6.92; Br, 42.26. Found: C, 50.83; H, 6.93; Br, 42.15.

(4-Methylenecyclohexyl)-methyl p-Toluenesulfonate.- According to the procedure of Marvel and Sekera (43), 126 g. (1.0 mole) of 1,4-methylenecyclohexanemethanol was caused to react with 210 g. (1.1 moles) of p-toluenesulfonyl chloride to yield 235 g. (83%) of (4-methylenecyclohexyl)-methyl p-toluenesulfonate, m.p. 60-62°C.

4-Methylenecyclohexanemethanal.-This compound was prepared using an adaptation of a procedure developed by Kornblum (44). Into a three-liter three-necked flask, equipped with a reflux condenser, mechanical stirrer, thermometer and a gas dispersion bubbler, were placed

126 g. (1.5 moles) of sodium bicarbonate and 500 ml. of dimethyl sulfoxide. Dry nitrogen was emitted through the gas bubbler, and the reaction mixture was heated to 150°C. At this temperature 197 g. (0.7 mole) of (4-methylenecyclohexyl)-methyl p-toluenesulfonate was added rapidly. After this addition was completed, the mixture was maintained at 150°C for 15 minutes and then cooled to room temperature. To the resulting slurry was added 600 ml. of distilled water, and the solution was then continuously extracted with 300 ml. of ethyl ether for 48 hours. The organic extract was dried for 24 hours over anhydrous sodium sulfate, and then the ether was removed by distillation at atmospheric pressure. The residue was distilled at reduced pressure through a 23-plate spinning-band column to yield 29 g. (33%) of 4-methylenecyclohexanemethanal, b.p. 60.5-61°C/11 mm., n_D^{20} 1.4892. Infrared analysis revealed the following absorption band assignable to the expected structure: 2720 cm.$^{-1}$(CHO), 1700 cm.$^{-1}$(CHO), 1650 cm.$^{-1}$(C=C), 890 cm.$^{-1}$($C=CH_2$).

Anal. Calcd. for $C_8H_{12}O$: C, 77.37; H, 9.74. Found: C, 77.21; H, 9.72.

Methyltriphenylphosphonium Bromide.-Using the method developed by Fields (15), 200 g. (0.76 mole) of triphenylphosphine, dissolved in 400 ml. of dry benzene, was caused to react with 100 g. (1.06 moles) of methyl bromide to yield 265 g. (97%) of methyltriphenylphosphonium bromide, m.p. 231-233°C; lit. (15) m.p. 233.5-234°C.

4-Methylene-1-vinylcyclohexane.-The procedure for the preparation of this compound was essentially the same as the one devised by Hauser and coworkers (45). A stirred slurry of 35.7 g. (0.1 mole) of methyltriphenylphosphonium bromide in 400 ml. of absolute ethyl ether, in a dry nitrogen atmosphere, was treated with 65 ml. of an approximately 15 per cent solution of *n*-butyl lithium in *n*-hexane. To the resulting reddish-orange solution of the triphenylphosphorusmethylide, at room temperature, was added a solution of 12.4 g. (0.1 mole) of 4-methylenecyclohexanemethanal in 30 ml. of dry ethyl ether. This mixture was stirred for 20 minutes, and 500 ml. of water were then added. Upon addition of the water, two layers were formed and the organic layer was removed. The aqueous layer was extracted with two 200-ml. portions of ether, and these extracts were combined with the organic layer. The combined ethereal portions were then dried for 24 hours over anhydrous sodium sulfate. The ether and *n*-hexane were removed by distillation through a 80-cm. vacuum-jacketed Vigreux column. The residue was distilled through a 23-plate spinning-band column under reduced pressure to yield 5 g. (41%) of 4-methylene-1-vinylcyclohexane, b.p. 70-71°C/58 mm. or 140-141°C/atmospheric, n_D^{20} 1.4674.

GLC analysis of the product revealed only one peak, and quantitative hydrogenation resulted in the reaction of 1.95 moles of hydrogen per mole of sample. The infrared spectrum of this compound has the following absorption bands which are assignable to the proposed structure: 1645 cm.$^{-1}$(C=C), 995 cm.$^{-1}$($CH=CH_2$), 910 cm.$^{-1}$($CH=CH_2$), 885 cm.$^{-1}$($C=CH_2$).

Anal. Calcd. for C_9H_{14}: C, 88.45; H, 11.55. Found: C, 88.58; H, 11.61.

2-Allylcyclohexanone.-This compound was prepared by following the procedure developed by VanderWerf and Lemmerman (47). Reaction of 220 g. (2.24 moles) of cyclohexanone with 246 g. (2.03 moles) of allyl bromide in the presence of sodium amide produced 128 g. (46%) of 2-allylcyclohexanone, b.p. 90-92°C/17 mm.; lit. (47) b.p. 90-92°C/17 mm.

2-Allyl-1-methylenecyclohexane.-In a two-liter three-necked flask, equipped with a stirrer, dropping funnel, reflux condenser and dry nitrogen cover, 117.1 g. (0.3 mole) of methylenetriphenylphosphonium bromide was dispersed in 800 ml. of dry tetrahydrofuran (THF). This mixture was cooled to -30°C by a dry ice-acetone bath and to it was added 186 ml. (0.31 mole) of a 1.65M solution of n-butyl lithium in n-hexane over a period of 30 minutes.

The resulting solution was warmed to room temperature, and then a solution of 41.4 g. (0.3 mole) of 2-allylcyclohexanone in 50 ml. of dry THF was added. The reaction mixture was then refluxed for 20 hours following which 895 ml. of solvent was removed by distillation at atmospheric pressure. The residue was taken up in 250 ml. of ethyl ether, and 200 ml. of water were then added. The resulting ether layer was removed, and the aqueous layer extracted with two 200-ml. portions of ether. The ethereal extracts were combined with the original organic layer and dried over anhydrous sodium sulfate for 12 hours. The volume of this solution was reduced to approximately 100 ml. by distillation at atmospheric pressure. To the residue was added 300 ml. of pentane, and this addition caused an immediate precipitation of a large amount of a white material (assumed to be triphenylphosphine oxide) which was removed by filtration. The filtrate was distilled at atmospheric pressure through a 30-cm. vacuum-jacketed Vigreux column to yield 27 g. (66%) of 2-allyl-1-methylenecyclohexane, b.p. 170-172°C, n_D^{20} 1.4721, D_4^{25} 0.8385. This product was found by GLC analysis to be 99+ per cent pure. This compound reacted with 2 moles of hydrogen per mole of sample when hydrogenated over a rhodium on alumina catalyst. Infrared analysis revealed the following absorption bands in agreement with the proposed structure:

1640 cm.$^{-1}$(C=C), 990 cm.$^{-1}$(CH=CH$_2$), 910 cm.$^{-1}$(CH=CH$_2$), 890 cm.$^{-1}$(C=CH$_2$).

Anal. Calcd. for $C_{10}H_{16}$: C, 88.16; H, 11.83. Found: C, 88.26; H, 11.85.

cis-1,3-Cyclopentanedicarboxaldehyde.-Into a five-liter, three-necked flask, equipped with a stirrer, condenser and addition funnel, was placed a solution of 37.6 g. (0.4 mole) of bicyclo[2.2.1]-2-heptene in 1.2 liters of acetone. To this solution at -15°C was added a solution of 75.8 g. (0.48 mole) of potassium permanganate and 57.6 g. (0.48 mole) of anhydrous magnesium sulfate in 1.8 liters of water. The aqueous solution was added at such a rate that the reaction temperature did not exceed -10°C. The mixture was then allowed to warm to room temperature and stirred for 21 hours. The manganese dioxide was removed by filtration, and the filtrate was poured into a five-liter flask. The volume of this solution was reduced to one liter by vacuum distillation (25 mm.). The residue was continuously extracted for 54 hours with diethyl ether. At the end of this period of time, the ethereal extract was removed and dried for 16 hours over anhydrous magnesium sulfate. The ether was removed from the solution by distillation at atmospheric pressure, and the residual fraction was distilled under reduced pressure through a 15-cm. Vigreux column to yield

18 g. of a colorless liquid, b.p. 87-92°C/3 mm. This material was redistilled through the same column to yield 13.8 g. (25%) of cis-1,3-cyclopentanedicarboxaldehyde, b.p. 69-71°C/1.3 mm., n_D^{23} 1.4725,2,4-dinitrophenylhydrazone derivative, m.p. 225-225.5°C (recrystallized from ethanol, m.p. 231.8-232.1°C); lit. (53) b.p. 74-75°C/1.5 mm., n_D^{25} 1.4759,2,4-dinitrophenylhydrazone derivative, m.p. 225-225.5°C.

cis-1,3-Divinylcyclopentane.-Using the same method as for the preparation of 2-allyl-1-methylenecyclohexane, 71.4 g. (0.2 mole) of methyltriphenylphosphorus bromide was caused to react with 132 ml. (0.2 mole) of a 1.5M solution of n-butyl lithium in n-hexane. The resulting solution was then caused to react with 12.6 g. (0.1 mole) of cis-1,3-cyclopentanedicarboxaldehyde to yield 6.2 g. (56%) of cis-1,3-divinylcyclopentane, b.p. 63-64°C/68 mm., $n_D^{24.5}$ 1.4532, D_4^{25} 0.8002. Infrared analysis revealed the following absorption bands: 3050 cm.$^{-1}$(C-H), 2920 cm.$^{-1}$(C-H), 1805 cm.$^{-1}$(overtone of 905 cm.$^{-1}$ band), 1620 cm.$^{-1}$(C=C), 1410 cm.$^{-1}$($CH=CH_2$), 987 cm.$^{-1}$($CH=CH_2$) and 905 cm.$^{-1}$($CH=CH_2$). The compound, which was found to be 99+ per cent pure by GLC analysis, took up 1.94 moles of hydrogen per mole of sample when hydrogenated over a rhodium on alumina catalyst. An NMR spectrum of this compound gave an integrated peak area ratio for sp^2 to sp^3 hydrogens of 8:12 (theoretical 9:12).

Anal. Calcd. for C_9H_{14}: C, 88.45; H, 11.54. Found: C, 88.29; H, 11.71.

n-Hexyltriphenylphosphonium Bromide.-The procedure for the preparation of this compound was essentially the same as the one used by Hauser and coworkers (45). The reaction of 229 g. (0.87 mole) of triphenylphosphine with 144 g. (0.87 mole) of n-hexyl bromide yielded 333 g. (90%) of n-hexyltriphenylphosphonium bromide, m.p. 198-200°C.

Anal. Calcd. for $C_{24}H_{28}PBr$: C, 67.4; H, 6.6; P, 7.3. Found: C, 67.3; H, 6.6; P. 7.2.

1-Heptene.-A two-liter flask and a 200-ml. flask were interconnected by means of a wide bore glass tube and the smaller flask connected to a suitable nitrogen source. The 200-ml. flask was charged with 20 g. (0.66 equivalent of formaldehyde) of paraformaldehyde, and then the entire system was placed under a nitrogen atmosphere. Into the larger flask was placed 42.7 g. (0.1 mole) of n-hexyltriphenylphosphonium bromide and 400 ml. of dry ethyl ether. To this suspension was added 80 ml. (0.13 mole) of a 15 per cent solution of n-butyl lithium in n-hexane by means of a hypodermic syringe. The resulting reddish-orange solution was allowed to stir for 30 minutes. A stream of dry nitrogen gas was emitted into the smaller flask with concurrent heating of the paraformaldehyde. The nitrogen flow rate was adjusted to approximately 10 ml. per minute.

The exit tube from the 200-ml. flask was adjusted so that the mixture of nitrogen and formaldehyde entered the larger flask at approximately two cm. above the liquid surface. The reaction was allowed to proceed until complete discoloration had been achieved (ca. 15 minutes). The reaction was subsequently quenched by the addition of 250 ml. of water. The organic layer was removed and the aqueous phase extracted with two 150-ml. portions of ethyl ether. The ethereal extracts were combined with the organic portion, and this solution was dried for 16 hours over anhydrous sodium sulfate. The ether and n-hexane were removed by distillation through a vacuum-jacketed 80-cm. Vigreux column and the residue distilled through a spinning-band column (23 theoretical plates) at atmospheric pressure to yield 4.6 g. (47%) of 1-heptene, b.p. 92-93°C, n_D^{20} 1.4013; lit. (54) b.p. 93.6, n_D^{20} 1.3998.

Styrene.-Using the same procedure as for the preparation of 1-heptene, part of 20 g. (0.66 equivalent of formaldehyde) of paraformaldehyde was caused to react with the phosphorane formed by the reaction of 43.3 g. (0.1 mole) of benzyltriphenylphosphonium bromide (45) with 80 ml. (0.13 mole) of a 15 per cent solution of n-butyl lithium in n-hexane. The yield of product was 6.6 g. (64%), b.p. 52-53°C/27 mm., n_D^{20} 1.5461; lit. (55) b.p. 52-53°C/28 mm., n_D^{20} 1.5462.

Pentamethylene-bis-(triphenylphosphonium bromide).- A mixture of 104.8 g. (0.4 mole) of triphenylphosphine, 46.0 g. (0.2 mole) of 1,5-dibromopentane and 250 ml. of dry dimethylformamide was refluxed with stirring under a dry nitrogen atmosphere for 16 hours, at which time 130 ml. of solvent was removed by distillation. The residue was allowed to cool and then poured into 500 ml. of dry benzene. The supernatant liquid was poured away from the resulting pasty material, and an additional 200 ml. of dry benzene were added to the paste whereupon immediate crystallization of the product occurred. The solid was broken up and, after washing on the filter with dry benzene and dry diethyl ether, was recrystallized from ethanol-isopropyl ether to yield 100 g. (66%) of pentamethylene-bis-(triphenylphosphonium bromide), m.p. 240-244°C.

Anal. Calcd. for $C_{41}H_{40}P_2Br_2$: C, 65.26; H, 5.34; P, 8.21. Found: C, 65.41; H, 5.38; P, 7.83.

1,6-Heptadiene.-The method for preparing 1-heptene was followed. Part of 20 g. (0.66 equivalent of formaldehyde) of paraformaldehyde was caused to react with the phosphorane formed by the reaction of 83 g. (0.11 mole) of pentamethylene-bis-(triphenylphosphonium bromide) with 150 ml. (0.24 mole) of an approximately 15 per cent solution of n-butyl lithium in n-hexane. The yield of product was 4.1 g. (45%), b.p. 89-90°C, n_D^{19} 1.4154; lit. (56) b.p. 90°C, n_D^{20} 1.4142.

Polymerizations

Intrinsic viscosities of all polymers were determined at 25°C in either benzene or chloroform. A discussion of the techniques and calculations involved may be found in any standard textbook of polymer chemistry.

The polymer melt temperature is defined as the lowest temperature at which a wet streak is left on a hot-stage upon pressing a sample of polymer with a spatula. This technique was adopted for the present work since most of the polymers incorporated some pendant double bonds, and if these materials are heated slowly over a long period of time, there is a high probability for crosslinking to occur.

Infrared studies were made on the polymers dissolved in either carbon tetrachloride or chloroform or on the solid polymers in the form of potassium bromide discs. In order to compare the infrared spectra of the polymers to their respective monomers, the spectra for the monomers were obtained on the pure compounds and on solutions of the monomers in carbon tetrachloride and chloroform.

The per cent cyclization calculation is based on the following equation:

$$\frac{100(dc-b)}{dc-b+a} = \text{per cent cyclization}$$

where:

a = number of sp^3 hydrogens in the saturated unit.
b = number of sp^3 hydrogens in the unsaturated unit.
c = number of sp^2 hydrogens in the unsaturated unit.
d = sp^3 to sp^2 hydrogens ratio as determined by NMR.

Since the experimental procedure was almost identical for all Zeigler catalyst initiated polymerizations, the experimental details are given for only one polymerization. The same situation applies to the gaseous boron trifluoride initiated polymerizations. The physical properties for the other polymers, except cis-1,3-divinylcyclopentane, obtained by these types of initiation are given in Tables 11, 12 and 13. The reaction conditions and yields can be found under the appropriate polymer numbers in Tables 7, 8 and 9 (Chap. II).

Poly-(1-methylene-4-vinylcyclohexane).-In a screw-cap vial which contained 5 ml. of high purity n-hexane was placed, by means of a micro-hypodermic syringe, 0.013 g. (0.11 millimole) of triethyl aluminum and 0.034 g. (0.17 millimole) of $TiCl_4$. After the catalyst had aged for 20 minutes at room temperature 1.8 g. (14.8 millimoles) of 1-methylene-4-vinylcyclohexane were added. All of the operations were, of course, carried out under a dry nitrogen atmosphere. The mixture was shaken well and

TABLE 11

PHYSICAL PROPERTIES OF SOLUBLE POLYMERS OF 1-METHYLENE-4-VINYLCYCLOHEXANE

Polymer Number	Polymer Melt Temperature (°C)	Intrinsic Viscosity	Elemental Analysis Calcd.(%)		Elemental Analysis Found (%)	
			C	H	C	H
7a	132	N.D.[*]	88.45	11.55	88.42	11.52
7b	104	0.09	88.45	11.55	88.29	11.69
7c	147	.11	88.45	11.55	N.D.	
7d	138	N.D.	88.45	11.55	88.42	11.56
7e	130	.06	88.45	11.55	N.D.	
7f	132	.08	88.45	11.55	88.44	11.49

[*] N.D. = not determined.

TABLE 12

PHYSICAL PROPERTIES OF SOLUBLE POLYMERS OF 1-ALLYL-2-METHYLENECYCLOHEXANE

Polymer Number	Polymer Melt Temperature (°C)	Intrinsic Viscosity	Elemental Analysis Calcd. (%)		Elemental Analysis Found (%)	
			C	H	C	H
8a	60	0.04	88.16	11.83	88.12	11.89
8b	65	0.04	88.16	11.83	N.D.	
8c	98	0.13	88.16	11.83	89.09	11.86
8e	102	0.13	88.16	11.83	N.D.	
8f	97	N.D.	88.16	11.83	88.14	11.87

*N.D. = not determined.

TABLE 13

PHYSICAL PROPERTIES OF SOLUBLE POLYMERS OF 4-VINYLCYCLOHEXENE

Polymer Number	Polymer Melt Temperature (°C)	Intrinsic Viscosity	Elemental Analysis			
			Calcd.(%)		Found (%)	
			C	H	C	H
9b	173	0.11	88.82	11.18	88.82	11.19
9c	168	0.07	88.82	11.18	88.69	11.22
9d	171	0.08	88.82	11.18	N.D.*	
9e	108	0.03	88.82	11.18	84.50	10.43
9f	91	0.04	88.82	11.18	88.71	11.10

*N.D. = not determined.

allowed to stand at room temperature for 14 days after which it was decomposed by pouring into 200 ml. of methanol. The polymer which precipitated was removed by filtration and dried for 16 hours at 50°C/1 mm.; yield 1.1 g. (61%). One gram of this material was placed in a Soxhlet extractor and continuously extracted with benzene for 40 hours. The extract was poured into 200 ml. of methanol, and the polymer immediately precipitated. This soluble portion was dried for 16 hours at room temperature/1 mm.; yield 0.1 g. (10%), polymer melt temperature of 104°C, intrinsic viscosity of 0.09 in benzene. The infrared spectra of both the soluble and insoluble fractions (run as potassium bromide discs) had the following absorption bands: 2950 $cm.^{-1}$(C-H), 1640 $cm.^{-1}$(C=C), 991 $cm.^{-1}$($CH=CH_2$), 910 $cm.^{-1}$($CH=CH_2$).

Anal. Calcd. for C_9H_{14}: C, 88.45; H, 11.55. Found: C, 88.29; H, 11.69.

Poly-(1-allyl-2-methylenecyclohexane).-Into a three-necked 100-ml. flask, equipped with a stirrer, reflux~~ed~~ condenser (connected to a mercury bubbler), and nitrogen inlet, was placed 5 g. (37 millimoles) of 1-allyl-2-methylenecyclohexane and 5 ml. of dry spectrograde dichloromethane. The reaction vessel was immersed in a dry ice-acetone bath, and dry nitrogen was emitted over the solution. The solution was stirred for 30 minutes at -70°C, and then the nitrogen flow was stopped, and gaseous boron trifluoride was emitted over the solution. The reaction flask was sealed off. After a reaction time of 46 hours, the flask was opened and its contents poured into 200 ml. of methanol. The polymer which precipitated was removed by filtration and then dried for 16 hours at room temperature/3 mm.; yield 2.2 g. (44%). This polymer was taken up in 20 ml. of chloroform, filtered and precipitated by pouring the solution into 200 ml. of methanol; yield 2.05 g. (94%), polymer melt temperature of 60°C, intrinsic viscosity of 0.4 in chloroform. The infrared spectrum of the soluble polymer (run in chloroform solution) revealed the following absorption bands: 2950 cm.$^{-1}$(C-H), 1640 cm.$^{-1}$(C=C), 995 cm.$^{-1}$($CH=CH_2$), 910 cm.$^{-1}$($CH=CH_2$). The soluble portion of this polymer was extracted with methanol on a Soxhlet extractor for 48 hours, and although the polymer melt temperature was increased to 82°C by the process, the degree of unsaturation was not appreciably reduced.

Anal. Calcd. for $C_{10}H_{16}$: C, 88.16; H, 11.83. Found: C, 88.12; H, 11.89.

Poly-(4-vinylcyclohexene).-Into a 50-ml. sample bottle was placed 10.8 g. (0.1 mole) of 4-vinylcyclohexene and 3 ml. of CH_2Cl_2. The bottle was immersed in a dry ice-acetone bath and dry nitrogen gas emitted over the solution. After 30 minutes at this temperature the vessel was sealed with a serum cap and 1 g. (7 millimoles) of boron trifluoride etherate was injected into the solution by means of a hypodermic syringe. The bottle was then removed from the bath and placed in a refrigerator (0°C) for 28 days. The contents of the vessel were poured into 200 ml. of methanol, and the polymer which precipitated was removed by filtration and dried in a vacuum oven. This material was taken up in 15 ml. of cold dichloromethane and then precipitated by pouring this solution into 200 ml. of acetone. The polymer was collected and vacuum dried at 60°C; yield 3.8 g. (35%), polymer melt temperature of 108°C, intrinsic viscosity of 0.03 in chloroform. The infrared spectrum of this polymer revealed absorption bands as follows: 2930 cm.$^{-1}$(C-H), 1630 cm.$^{-1}$(C=C), 990 cm.$^{-1}$($CH=CH_2$), 910 cm.$^{-1}$($CH=CH_2$). The NMR spectrum shows an sp^2 to sp^3 hydrogens ratio of 1:28. The elemental analysis on the soluble polymer was in serious error, but this was probably due to some occluded material since dissolving the polymer and reprecipitating it did reduce this error.

Anal. Calcd. for C_8H_{12}: C, 88.82; H, 11.18 ~~11.38~~.
Found (first determination): C, 82.81; H, 10.34.
Found (second determination): C, 84.50; H, 10.43.

Poly-(cis-1,3-divinylcyclopentane).-The procedure for the polymerization of this compound was essentially the same as the one used for the polymerization of 1-methylene-4-vinylcyclohexane. The catalyst solution was composed of 0.8 ml. of a 1M solution of triisobutyl aluminum in n-heptane and 1.6 ml. of a 0.5M solution of titanium tetrachloride in n-heptane. To this solution was added an additional 1.4 ml. of n-heptane and 0.65 g. (5.2 millimoles) of cis-1,3-divinylcyclopentane. After the reaction had proceeded at room temperature for 72 hours, the mixture was decomposed with methanol. The total yield of polymer was 0.24 g. (38%) of which approximately 65 per cent was soluble in hot cyclohexane. The soluble fraction had a polymer melt temperature of 116°C, and an infrared spectrum of this compound revealed the following absorption bands: 2920 $cm.^{-1}$(C-H), 1620 $cm.^{-1}$(weak), 987 $cm.^{-1}$(weak), 905 $cm.^{-1}$(med.).

Anal. Calcd. for C_9H_{14}: C, 88.45; H, 11.54. Found: C, 87.89; H, 11.21.

CHAPTER IV

SUMMARY

4-Methylene-1-vinylcyclohexane, 1-allyl-2-methylenecyclohexane and cis-1,3-divinylcyclopentane have been prepared by condensation of the appropriate aldehydes with methylidenetriphenylphosphorane via the Wittig reaction.

4-Vinylcyclohexene, 4-methylene-1-vinylcyclohexane and 1-allyl-2-methylenecyclohexane were polymerized by both metal alkyl coordination catalyst and cationic initiators. The polymers derived from these monomers invariably contained polymeric fractions (10-100%) which were soluble in a variety of organic solvents. The soluble polymers usually incorporated some open chain unsaturated groups, and the percentages of these units were determined from the sp^2 to sp^3 hydrogens ratios as revealed by the NMR spectra. Calculations based on these same ratios indicated that from 45 to 90 per cent of the monomer units incorporated in the soluble polymers had undergone cyclization during the polymerizations. The highest percentages of cyclization occurred when the monomers were initiated with metal alkyl coordination catalyst. cis-1,3-Divinylcyclopentane was polymerized by initiation with the system triisobutyl aluminum-titanium tetrachloride to yield a polymer of which 65 per cent was soluble in hot cyclohexane.

The procedure developed by Wittig for the synthesis of olefins has been extended to include the reaction of alkyltriphenylphosphoranes with gaseous formaldehyde to yield terminal olefins. 1-Heptene, styrene and 1,6-heptadiene were prepared by this new method.

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BIOGRAPHICAL SKETCH

Marion L. Miles was born on September 5, 1929, at Columbus, Georgia. He attended elementary and secondary schools in Columbus, Georgia, and graduated from Jordan High School in 1946. He spent two years in the United States Army serving at Aberdeen Proving Ground, Maryland, and Germersheim, Germany. The author attended Georgia Southwestern College from September, 1952, until June, 1953, and received the degree of Bachelor of Science in Chemistry from the University of Georgia in June, 1957. He entered the Graduate School at the University of Georgia in September, 1957, and received the degree of Master of Science in August, 1959. In the Fall of 1959 he enrolled in the Graduate School at the University of Florida.

The author is a member of Gamma Sigma Epsilon, Chemistry Professional Fraternity, Pi Mu Epsilon, Mathematics Honorary Fraternity and the American Chemical Society.

The author is married to the former Hester Gail Stevens and is the father of two children, Marion L. Miles, Jr., and Blair Stevens Miles.

This dissertation was prepared under the direction of the chairman of the candidate's supervisory committee and has been approved by all members of that committee. It was submitted to the Dean of the College of Arts and Sciences and to the Graduate Council, and was approved as partial fulfillment of the requirements for the degree of Doctor of Philosophy.

April 20, 1963

Dean, College of Arts and Sciences

Dean, Graduate School

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